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***In Situ* High-energy X-ray Diffraction for Advanced Material Discovery and Design**

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It has been widely accepted that the structure, chemical, and physical defects of materials are critical factors to determine the performance of devices using such materials. A comprehensive understanding of the structure-property relationship of materials can provide valuable insight for the discovery and rational design of advanced materials with improved performance. The accomplishment of this challenging task will need critical support from state-of-the-art characterization techniques such as *in situ* high-energy x-ray diffraction.

For instance, LiFePO_4 was first reported by Goodenough and coworkers as a potential positive electrode material for lithium ion batteries in 1997 [1]. Because of its low electronic conductivity, the full potential of LiFePO_4 for lithium ion batteries was not unlocked until Chiang and coworkers reported that high rate application of LiFePO_4 can be achieved by chemical doping of metal metals supervalent to Li in nanostructured LiFePO_4 [2]. However, the mechanism of the performance improvement is still under debate [3, 4].

In this work, *in situ* high-energy x-ray diffraction technique was used to investigate the phase formation and defect evolution of LiFePO_4 during solid state synthesis. The *in situ* experiment showed that LiFePO_4 phase started to form at a temperature as low as 200°C, and a pure LiFePO_4 was obtained at about 300°C. It was also found that impurity phases, which were identified as a mixture of Fe_2P and Fe_3P , started to appear when the LiFePO_4 sample was baked at a temperature above 400°C. Electrochemical data showed that LiFePO_4 synthesized at <400°C exhibit poor electrochemical activity while those samples prepared at >500°C have great performance. With the combination of *in situ* data and electrochemical data, we realized that the $\text{Fe}_2\text{P}/\text{Fe}_3\text{P}$ impurity phases are critical for the performance improvement.

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